JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 85, NO. B12, PAGES 6937-6943, DECEMBER 10, 1980

Studies in Synthetic Carbonatite Systems: Solidus Relationships for $CaO-MgO-CO_2-H_2O$ to 40 kbar and $CaO-MgO-SiO_2-CO_2-H_2O$ to 10 kbar

A. L. BOETTCHER

Institute of Geophysics and Planetary Physics and Department of Earth and Space Sciences University of California, Los Angeles, California 90024

J. K. ROBERTSON

Science Research Laboratory, Department of the Army, HG., U.S. Military Academy, West Point, New York 10996

P. J. WYLLIE

Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637

The system $CaO-MgO-SiO_2-CO_2-H_2O$ is an important model for many igneous and metamorphic processes, including the generation and differentiation of carbonatite and associated silicate magmas. We have experimentally established the vapor-saturated solidus for the system $CaO-MgO-CO_2-H_2O$ from 595°C/1 kbar to <500°C/40 kbar, about 25°C lower than the corresponding temperatures for the $CaO-CO_2-H_2O$ system. Brucite replaces periclase on the vapor-saturated solidus at about 750 bars pressure, remaining as the stable phase to pressures of at least 40 kbar; no dolomite or magnesite was encountered. At a pressure between 35 and 40 kbar, the assemblage portlandite + brucite + aragonite + vapor changes to one containing phase W, a previously unreported Ca-Mg carbonate. At 20 kbar, the vapor-saturated liquid contains at least 24 wt % H_2O. The vapor-saturated solidus for the system $CaO-MgO-SiO_2-CO_2-H_2O$ ranges from 613°C/1 kbar to 565°C/10 kbar, experimentally indistinguishable from that for $CaO-MgO-CO_2-H_2O$, about 10°C lower than that for $CaO-CO_2-H_2O$, and about 25°C lower than that for $CaO-SiO_2-CO_2-H_2O$. In the quinary system, monticellite is replaced by dellaite and an unidentified silicate on the vapor-saturated solidus above 4.1 kbar. MgO-poor liquids are similar in composition to the magma from which the Magnet Cove calcite carbonatite crystallized. More magnesian magmas would produce dolomite at moderate depths, such as at Alnö Island.

INTRODUCTION

The system $CaO-MgO-SiO_2-CO_2-H_2O$ is an important model for several different geological problems, including the metamorphism of siliceous dolomites, the effect of CO_2 and H_2O on the melting of mantle peridotite, the petrogenetic links between kimberlite and carbonatitic magmas, and the differentiation of carbonatites from associated silicate magmas at crustal pressures. Our present study is concerned with the low-temperature synthetic carbonatite magmas, and their possible relationships to silicate magmas.

George C. Kennedy was responsible for early research in parts of this system, as in so many others. His pioneering work on the properties of H_2O and CO_2 is represented, for example, by study of the binary system H_2O-CO_2 to 3 kbar [*Takenouchi and Kennedy,* 1964]. Another investigation determined the solubility of calcite in solutions of $H_2O + CO_2$ to 1.4 kbar [*Sharp and Kennedy,* 1965]. Our efforts were directed toward determining the conditions of melting and the minerals coexisting with liquid.

EXPERIMENTAL PROCEDURES

Starting Materials

Forsterite synthesized from gels [*Luth and Ingamells,* 1965] and reagent-grade MgO, $Mg(OH)_2$, and $Ca(OH)_2$ and Matthey 'Specpure' $CaCO_3$ (calcite) were mixed in the desired proportions by placing weighed proportions into a mechanical mixer. Treatment of the reagents was as follows: $CaCO_3$ was heated 530°C for 48 hours. $Ca(OH)_2$ (portlandite) was dried at 240°C for 2 hours. MgO (periclase) was fired at about 1200°C for 24 hours. $Mg(OH)_2$ was dried at 150°C for 4 hours. A natural dolomite from Gabbs, Nevada [*Goldsmith and Heard,* 1961], was used in some experiments.

Equipment and Methods

Experiments were conducted in cold-seal pressure vessels and in piston-cylinder apparatus. Starting mixes with and without H_2O were encapsulated in welded gold tubing, and external chromel-alumel thermocouples were used to measure temperature. Some of the experiments at and below 1 kbar pressure used both an internal and external thermocouple; the latter consistently indicated temperatures about 15°C higher because we did not use filler rods in the cold-seal vessels [see *Boettcher and Kerrick,* 1971]. The temperatures in Table 1 are those of the external thermocouple and have been revised downward 15°C. These revised results are uncertain by about ±5°C. The temperatures for the experiments in the piston-cylinder are probably accurate to ±5°C, neglecting the pressure effect on the thermocouples. Our experimental procedures have been described in detail for the piston-cylinder apparatus [*Boettcher and Wyllie,* 1968].

Identification of Phases

The following abbreviations are used: aragonite, $CaCO_3$ (Ar); $Mg(OH)_2$ (MH); calcite, $CaCO_3$ (CC); calciochondrodite, $Ca_5(SiO_4)_2(OH)_2$ (Ch); dellaite, $Ca_{12}Si_6O_{22}(OH)_4$ (Y); dolomite, $CaMg(CO_3)_2$ (Do); forsterite, Mg_2SiO_4 (Fo); liquid

Paper number 80B0707.
0148-0227/80/080B-0707$01.00

TABLE 1. Definitive Experiments in the System CaO-MgO-CO_2-H_2O

Run	Composition, wt % Solids CC	CH	MH	P	Do	H_2O	Temp., °C	Pressure, kbar	Time, hours	Results X ray	Phases at P and T of Run
						Cold-Seal Pressure Vessel					
503	46	46		8		25	590	0.75	20	CC,CH,P	CC,CH,P,V
504	40	40	20			25	590	0.75	20	CC,CH,MH	CC,CH,MH,V
407	40	40	20			30	610	0.75	20	CC,CH,MH	CC,MH,L,V
408	46	46		8		30	610	0.75	20	CC,CH,P	CC,P,L,V
415	40	40	20			25	610	0.75	264	CC,CH,MH	CC,MH,P,L,V
414	46	46		8		25	610	0.75	264	CC,CH,P	CC,P,L,V
740	46	46		8		18	595	0.85	360	CC,CH,MH,P	CC,MH,P,L,V
748	40	40	20			19	595	0.85	360	CC,CH,MH	CC,MH,L,V
756			50	50		25	595	0.85	360	MH	MH,V
739	46	46		8		18	615	0.85	288	CC,CH,P	CC,P,L,V
747	40	40	20			19	615	0.85	288	CC,CH,P	CC,P,L,V
755			50	50		26	615	0.85	288	P,(MH)	P,V
501	40	40	20			25	585	1.0	20	CC,CH,MH	CC,CH,MH,V
502	46	46		8		25	585	1.0	20	CC,CH,MH	CC,CH,MH,V
405	40	40	20			30	600	1.0	22	CC,CH,MH	CC,MH,L,V
406	46	46		8		30	600	1.0	22	CC,CH,MH	CC,MH,L,V
744	46	46		8		24	590	1.0	384	CC,CH,MH	CC,CH,MH,V
752	40	40	20			24	590	1.0	384	CC,CH,MH	CC,CH,MH,V
760			50	50		24	590	1.0	384	MH	MH,V
743	46	46		8		22	600	1.0	433	CC,CH,MH	CC,MH,L,V
751	40	40	20			22	600	1.0	433	CC,CH,MH	CC,MH,L,V
759			50	50		35	600	1.0	433	MH	MH,V
742	46	46		8		21	610	1.0	432	CC,CH,(MH),P	CC,P,L,V
750	40	40	20			22	610	1.0	432	CC,CH,(MH),P	CC,P,L,V
758			50	50		30	610	1.0	432	MH,P	P,V
741	46	46		8		22	630	1.0	432	CC,CH,(MH),P	CC,P,L,V
749	40	40	20			26	630	1.0	432	CC,CH,(MH),P	CC,P,L,V
757			50	50		24	630	1.0	432	MH,P	P,V
260	44	22			34		565	4.1	24	CC,CH,MH	CC,CH,MH,V
261	37	37	26				565	4.1	24	CC,CH,MH	CC,CH,MH,V
262	46	46	8				565	4.1	24	CC,CH,MH	CC,CH,MH,V
263	30	62	8				565	4.1	24	CC,CH,MH	CC,CH,MH,V
110	46	46		8		19	586	4.1	0.5	CC,CH,MH	CC,CH,MH,V
112	69	23		8		22	586	4.1	0.5	CC,CH,MH	CC,CH,MH,V
114	69	23		8		21	598	4.1	0.5	CC,CH,MH	CC,MH,L,V
245	37	37		8			600	4.1	23	CC,CH,P	CC,CH,P,L
247	70	15		15			600	4.1	23	CC,CH,P	CC,CH,P,L
246	30	62		8			600	4.1	23	CC,CH,P	CC,CH,P,L
248	46	46		8			600	4.1	23	CC,CH,P	CC,CH,P,L
210	44	22			34		615	4.1	13	CC,CH,MH	CC,CH,MH,L
212	46	46	8				615	4.1	13	CC,CH,MH	CC,CH,MH,L
213	30	62	8				615	4.1	13	CC,CH,MH	CC,CH,MH,L
115	69	23		8		20	618	4.1	2	CC,CH,MH	CC,MH,L,V
111	46	46		8		25	672	4.1	0.5	CC,CH,MH	CC,MH,L,V
113	69	23		8		20	672	4.1	0.5	CC,CH,MH	CC,MH,L,V
						Piston-Cylinder Apparatus					
707	69	23		8		18	565	10.0	24	CC,CH,MH	CC,CH,MH,V
709	69	23		8		21	575	10.0	24	CC,CH,MH	CC,MH,L,V
331	44	22			34		655	10.0	24	CC,CH,MH	CC,CH,MH,L
438	75		25			31	780	10.2	14	CC,MH	CC,MH,V
439	75		25			30	850	10.3	11	CC,MH	CC,P,L,V
154	69	23		8		23	552	15.0	3	Ar,CH,MH	Ar,CH,MH,L,V
149	46	46		8		23	557	15.5	9	Ar,CH,CC,MH	Ar,MH,L,V
148	46	46		8		23	542	15.0	1	Ar,CH,MH	Ar,CH,MH,V
443	75		25			*	850	15.8	21	CC,MH	CC,MH,L,V
193	30	62		8		23	529	20.0	2	Ar,CH,MH	Ar,CH,MH,V
192	30	62		8		24	539	20.0	2	Ar,CH,MH	Ar,CH,MH,V
175	46	46		8		26	540	20.0	2	Ar,CH,MH	Ar,CH,MH,V
167	44	22			34	19	545	20.0	1	Ar,CH,MH	Ar,CH,MH,(L?)
172	46	46		8		24	550	20.0	2	Ar,CH,MH	Ar,CH,MH,L
173	46	46		8		25	555	20.0	2	Ar,CH,MH	Ar,CH,MH,L
191	30	62		8		24	555	20.0	2	Ar,CH,MH	Ar,CH,MH,L
174	46	46		8		24	570	20.0	2	Ar,CH,MH	Ar,CH,MH,L
440	75		25			29	802	20.3	20	CC,MH	CC,MH,V
466	75		25				839	21.6	17	MH,Do	MH,Do
470			70		30		845	21.3	6	MH,Do	MH,Do
467			75		25		850	21.3	19	MH,Do,P	MH,P,L,V
441	75		25			26	850	21.0	18	CC,MH	CC,P,L,V
444	75		25			8	853	20.6	8	CC,MH	CC,P,L,V

TABLE 1. (Continued)

Piston-Cylinder Apparatus (Continued)										
170	46	46		8	23	505	25.0	180	Ar+CH+MH	Ar+CH+MH+V
169	46	46		8	23	515	25.0	240	Ar+CH+MH	Ar+CH+MH+L(?)
150	46	46		8	24	525	25.0	300	Ar+CH+MH	Ar+CH+MH+L(?)
151	46	46		8	22	535	25.0	180	Ar+CH+MH	Ar+CH+MH+L(?)
178	40	40	20		9	540	25.0	120	Ar+CH+MH	Ar+CH+MH+L(?)
152	46	46		8	25	544	25.0	180	Ar+CH+MH	Ar+CH+MH+L(?)
177	69	13	18		9.5	546	25.0	180	Ar+CH+MH	Ar+CH+MH+L(?)
176	46	46		8	40	547	25.0	180	Ar+CH+MH	Ar+CH+MH+L(?)
153	46	46		8	24	555	25.0	180	Ar+CH+MH	Ar+CH+MH+L(?)
155	69	23		8	24	575	25.0	180	Ar+CH+MH	Ar+CH+MH+L
171	46	46		8	24	595	25.0	240	Ar+CH+MH	Ar+CH+MH+L
204	30	62		8	27	499	30.0	115	Ar+CH+MH	Ar+CH+MH+V
203	30	62		8	28	509	30.0	100	Ar+CH+MH	Ar+CH+MH+L
202	30	62		8	27	520	30.0	125	Ar+CH+MH	Ar+CH+MH+L
445	75		25		5	853	31.7	6	CC,Ar,MH	CC,P,L,V
446	75		25			852	31.7	7	CC,Ar,MH	CC,P,L,V
222	23	69		8	56	500	35.0	130	Ar+CH+MH	Ar+CH+MH+V
227	23	69		8	35	510	35.0	150	Ar+CH+MH	Ar+CH+MH+L
200	30	62		8	26	505	40.0	100	W+CH+MH	W+CH+MH+L(?)
201	30	62		8	25	515	40.0	180	W+CH+MH	W+CH+MH+L(?)

Ar, aragonite; CC, calcite; CH, portlandite; Do, dolomite; L, liquid; MH, brucite; P, periclase; V, vapor; W, unidentified carbonate.
Phase in parentheses indicates small proportion.
*14% oxalic acid.

(L); periclase MgO (P); monticellite, $CaMgSiO_4$ (Mo); portlandite, $Ca(OH)_2$ (CH); unknown carbonate (W); unknown silicate (T); and vapor (V).

Liquids in these systems do not quench to glasses but to aggregates of crystalline material identifiable by petrographic methods. For this reason, we were not able to reverse these melting experiments by running the products in the liquid-absent fields. Descriptions of some of the crystalline phases encountered, together with detailed criteria for the recognition of liquids and vapors, have been adequately discussed elsewhere [*Wyllie and Tuttle,* 1960; *Boettcher and Wyllie,* 1968; *Wyllie and Boettcher,* 1969]. In addition, brucite grown in the presence of a liquid occurs as rounded grains or, at the higher pressures, as hexagonal grains with prominent basal faces. Brucite in subsolidus assemblages and brucite quenched from vapor occurs as small, irregular grains or as sheafs of acicular crystals. All crystalline phases were identified microscopically and by X ray diffraction.

Recognition of the former presence of a vapor phase at the lower pressures was by examination of charge and capsule or by application of the phase rule, as outlined in *Wyllie and Boettcher* [1969]. However, at pressures above about 10 kbar, solids precipitated from the vapors during quenching in amounts sufficient to permit reliable detection of former vapor. In lower-pressure runs where quenched vapor could be recognized, the deposits consisted of colorless to light brown, isotropic (or amorphous) aggregates. With increasing solubility of solids in the vapor at successively higher pressures, the deposits became darker brown and more abundant. At the highest pressures investigated, the quenched liquids remained distinctive from quenched vapors, and no critical end-points were encountered [*Boettcher and Wyllie,* 1969]. The solubility of solids in the vapor in the system $CaO-MgO-CO_2-H_2O$ appears to be greater than in the system $Ca-CO_2-H_2O$ [*Wyllie and Boettcher,* 1969] but less than in the system $CaO-SiO_2-CO_2-H_2O$ [*Boettcher and Wyllie,* 1969].

EXPERIMENTAL RESULTS

Melting Relationships at Low Pressures in the System $CaO-MgO-CO_2-H_2O$

As indicated in Table 1 and Figure 1, brucite is the stable crystalline magnesian phase in equilibrium with liquid at pressures at least as low as 1 kbar, whereas periclase is the phase stable at 500 bars pressure [*Wyllie,* 1965]. Wyllie suggested that brucite would become stable on the solidus relative to periclase at about 1 kbar pressure (see Figure 1). In the present study, runs 744, 752, 743, and 751 confirm that brucite is the stable crystalline magnesian phase at 1 kbar when either brucite or periclase is used in the starting mixes. Because brucite and periclase are nearly stoichiometric $Mg(OH)_2$ and MgO, respectively, and the vapor phase is nearly pure H_2O under these experimental PT conditions, the brucite-periclase transition in the system $CaO-MgO-CO_2-H_2O$ is nearly coincident with this transition in the system $MgO-H_2O$. Our results in the latter system using equal weights of brucite and periclase in the starting mixes (Table 1) provide brackets at 595°–615°C and 600°–610°C at 850 and 1000 bars, respectively. These results agree with those of *Barnes and Ernst* [1963] within experimental error. Runs 743 and 750 at 1 kbar and 747 and 740 at 850 bars confirm that the brucite-periclase transition in the system $CaO-MgO-CO_2-H_2O$ is at a temperature similar to that in $MgO-H_2O$.

Additional runs at 750 and 850 bars were performed to obtain a closer bracket on the pressure of the invariant point at which brucite replaces periclase on the solidus. Both brucite and periclase were used in the starting mixes in an attempt to reverse the reaction. In runs of 20 hours duration at 750 bars (503 and 504), the product was governed by whether brucite or periclase was used in the starting mixes. In runs 740 and 748 at 850 bars, 15-day runs produced some brucite in the periclase-bearing mix, but no periclase was produced with the brucite-bearing mix. These data suggest that the invariant point is near 750 bars. Run 407 at 750 bars contains brucite although it is at a temperature above the stability curve for the periclase-brucite reaction, as indicated in runs 750 and 758 at 1 kbar. This indicates that the run duration in 407 (20 hours) is insufficient.

Melting Relationships at High Pressures in the System $CaO-MgO-CO_2-H_2O$

Melting relationships in this quaternary system were investigated at pressures above 1 kbar to locate the vapor-saturated solidus to pressures of 40 kbar and to determine what phases coexist with H_2O-saturated and H_2O-unsaturated liquids. The

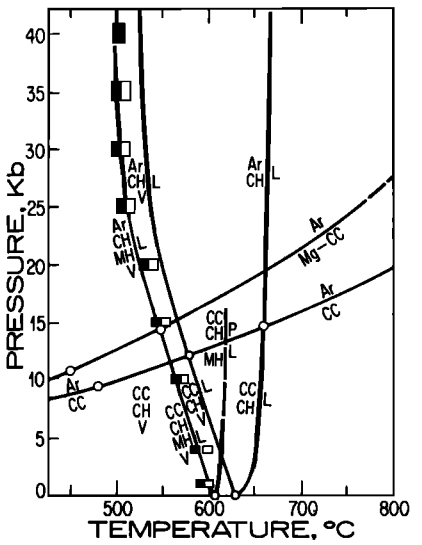

Fig. 1. Pressure-temperature projection for $CaO-MgO-CO_2-H_2O$ and bounding systems. Abbreviations: Ar, aragonite; CC, calcite; CH, portlandite; Do, dolomite; L, liquid; MH, brucite; P, periclase, and V, vapor. The quaternary solidus is determined by results in Table 1, shown here as rectangles. Melting reactions in the system $CaO-CO_2-H_2O$ are modified from *Wyllie and Boettcher* [1969]. The calcite-aragonite transitions are from *Goldsmith and Newton* [1969].

results of these experiments appear in Figure 1 and Table 1. The vapor-saturated solidus for the system $CaO-CO_2-H_2O$, presented in this figure for comparison, is lower by 15°C at pressures up to 4 kbar than originally shown by *Wyllie and Boettcher* [1969] to account for the problem in measurement of temperatures discussed earlier. The quaternary solidus was bracketed between 586° and 598°C at 4.1 kbar (runs 112 and 114), in agreement with the value of 590°–610°C at 4.0 kbar determined by M. Carapezza [see *Wyllie*, 1965, p. 105]. At a pressure of 1 kbar, our brackets at 595° and 610°C agree with the preliminary results of *Wyllie and Tuttle* [1960*b*] at 620°C. As in the ternary system, no inflection was noted, within experimental limits, where the solidus intersects the CC ⇆ Ar transition curve [*Boettcher and Wyllie*, 1968]. Although these data do allow some inflection in the solidus, it appears that the increase in density resulting from the transition to aragonite is nearly compensated by the decrease in entropy, resulting in no detectable change in the dP/dT slope. Our experimental results (runs 148, 149, and 154) in this system (Figure 1) are consistent with those for the transition of magnesium-saturated calcites to aragonite reported by *Goldsmith and Newton* [1969]. The aragonite in runs 445 and 446 is produced when the liquid is quenched through the stability field of aragonite. As noted in the systems $CaO-CO_2-H_2O$ [*Wyllie and Boettcher*, 1969] and $CaO-SiO_2-CO_2-H_2O$ [*Boettcher and Wyllie*, 1969], portlandite apparently undergoes a nonquenchable phase transition between 15 and 20 kbar, as subsolidus portlandite quenched from above this pressure is complexly twinned, compared with untwinned portlandite quenched from lower pressures. At a pressure between 35 and 40 kbar, the assemblage portlandite + brucite + aragonite + vapor (or liquid) changes to one containing phase W, a previously unreported phase, presumably a hydrous Ca-Mg carbonate (see Table 2). *Wyllie* [1965] predicted that dolomite would coexist with liquid at high pressures in this system. However, runs to temperatures well above the solidus over the pressure range of interest, using a variety of compositions and phases as starting materials, failed to produce such an assemblage.

Electron microprobe analyses of aragonite crystals grown at 25 kbar and 575°C (run 155) revealed a surprisingly low Mg content of less than 100 ppm. Even this high pressure is insufficient to stabilize Mg ions in the nine fold coordination sites of the aragonite structure. The unit-cell parameters determined from X ray diffraction powder patterns of aragonite from runs spanning the PT range investigated show no detectable departure from those for Mg-free aragonite.

Run 191 provides an estimate of the H_2O content of the eutectic melt at 20 kbar pressure; at least 24 wt % H_2O is insufficient to saturate the liquid, as indicated by the absence of vapor. Although the bulk composition is not that of the eutectic, run 149 indicates that the $Ca(OH)_2/CaCO_3$ ratio of the eutectic is greater than unity at 15.5 kbar, as it is at pressures as low as 750 bars (run 408).

As shown in Figure 1, brucite is stable at the temperature of the beginning of melting under vapor-saturated conditions to pressures of at least 40 kbar. Note in runs 439, 441, 444, and 445 that periclase present at run conditions inverted to brucite during the quench. In run 446, with no H_2O in excess of that in brucite, some of the periclase did not invert to brucite.

Thus these experimental results indicate that brucite is the stable crystalline magnesian phase to pressures in excess of 20 kbar, and dolomite and magnesite do not coexist with a liquid phase in any part of the PT range investigated.

Melting Relationships to 10 kbar in the System $CaO-MgO-SiO_2-CO_2-H_2O$

Previous studies in this system at 1 kbar pressure by *Franz* [1965] and *Franz and Wyllie* [1967] delineated the conditions under which phases such as brucite, monticellite, merwinite, and forsterite coexist with liquids and vapors; no dolomite or magnesite was encountered. The reaction representing the vapor-saturated solidus studied by these workers is

$$CC + CH + MH + Mo + V \leftrightarrows L$$

TABLE 2. X Ray Diffraction Peaks and Optical Properties of Unidentified Phase W

d, Å	I/I_0
7.20	M
4.175	M
3.637	VS
3.510	M
3.322	M
3.028	M
2.969	W
2.908	W
2.827	W
2.751	M
2.690	S
2.568	W
2.386	VS
2.270	VS
2.209	S
2.091	W
2.012	S
1.996	M
1.801	S

Additional peaks may be concealed by those of MH and CH.
Comments: Euhedral, six-sided crystals; biaxial (+); $2V \sim 40°$; $n_\alpha = 1.631 \pm 0.003$; $n_\gamma = 1.676 \pm 0.003$.

TABLE 3. Experiments in the System $CaO-MgO-SiO_2-CO_2-H_2O$

Run	Composition, wt % Solids CC-CH	Solids Fo	H_2O	Temp., °C	Pressure, kbar	Time, hours	Phase at P and T of Run
				Cold-Seal Vessel			
208*	20–80	10		590	1.0	4	CC,CH,MH,Mo,V
209*	20–80	10		598	1.0	4	CC,CH,MH,Mo,V
220*	20–80	10		607	1.0	4	CC,CH,MH,Mo,V
285*	20–80	10	20	610	1.0	4	CC,CH,MH,Mo,V
223*	20–80	10		616	1.0	4	CH,MH,Mo,L,V
224*	20–80	10	25	616	1.0	4	CH,MH,Mo,L,V
709*	20–80	10	26	615	1.0	240	CH,P,Mo,L,V
157*	50–50	10	17	586	4.1	30	CC,CH,MH,Mo,V
158*	20–80	30	17	586	4.1	27	CC,CH,MH,Mo,V
159*	20–80	10	18	586	4.1	27	CC,CH,MH,Mo,V
160*	50–50	10	18	586	4.1	27	CC,CH,MH,Mo,V
161*	20–80	10	19	595	4.1	144	CH,MH,Mo,L,V
162*	20–80	30	18	595	4.1	144	CH,MH,Mo,L,V
163*	50–50	10	19	595	4.1	144	CC,MH,Mo,L,V
164*	50–50	30	18	595	4.1	144	CC,MH,Mo,L,V
				Piston-Cylinder Apparatus			
214	15–85	20	26	570	8.0	6	CC,CH,MH,Y,V
215	15–85	20	27	580	8.0	5	CH,MH,Y,L,V
194	20–80	30	25	580	7.0	5	CC,MH,Y,L,V
196	20–80	30	26	591	7.0	7	CC,MH,Y,L,V
197	20–80	30	32	575	10.0	3	
				550	10.0	5	CC,CH,MH,Y,V
195	20–80	30	27	560	10.0	5	CC,CH,MH,Y,V
187	50–50	30	22	570	10.0	5	CC,CH?,MH,T,L,V
188	50–50	30	23	580	10.0	5	CC,MH,T,L,V
216	15–85	20	28	572	9.0	5	CH,MH,Y,L,V
				Cold-Seal Vessel			
179	50–50	10	24	700	4.1	12	CC,MH,Mo,L,V
180	50–50	30	10	700	4.1	12	CC,MH,Mo,L,V
181	70–30	30	26	700	4.1	12	CC,MH,Mo,L,V
182	70–30	30		700	4.1	12	CC,CH,MH,Mo,L
183	50–50	30		750	4.1	13	CC,CH,P,Mo,L
184	70–30	30		750	4.1	13	CC,CH,P,Mo,L

CC, calcite; CH, portlandite; Fo, forsterite; L, liquid; MH, brucite; Mo, monticellite; P, periclase; T, unknown silicate; V, vapor; Y, dellaite.

*Two-stage run.

We extended this investigation to 10 kbar; the results are listed in Table 3 and are illustrated in Figure 2. At pressures above 4.1 kbar, monticellite is replaced by dellaite and an unidentified silicate (phase T). Our results are compared with earlier determinations of the vapor-saturated solidi in the systems $CaO-CO_2-H_2O$ and $CaO-SiO_2-CO_2-H_2O$ in this same figure. The quinary curve appears to be somewhat lower in temperature, but the differences are within experimental uncertainty.

Comparing Figures 1 and 2, adding SiO_2 to the system $CaO-MgO-CO_2-H_2O$ does not significantly change the temperature of the beginning of melting. The brackets for the quaternary curve at 1, 4.1, and 10.0 kbar are 590°–600°C, 586°–598°C, and 565°–575°C, respectively, compared to 610°–616°C, 586°–596°C, and 560°–570°C, respectively, for the quinary curve. This simply reflects the very small solubility of SiO_2 in these low-temperature, carbonate-rich liquids. The bracket of the quinary reaction at 1 kbar is within experimental uncertainty of the value reported by *Franz and Wyllie* [1967]. SiO_2 probably is not significantly soluble in calcite, portlandite, or brucite, so that the relative temperatures of the quaternary (SiO_2-free) and quinary reactions depend upon the relative solubility of SiO_2 in the quinary liquid and vapor. If SiO_2 is more soluble in the vapor, then the quinary reaction can be at a higher temperature, which is permitted by our data.

Comparing runs 223, 224, and 709 in Table 3 shows that periclase is stable at 615°C and 1 kbar, but run durations in excess of 4 hours are required to convert the brucite in the starting material because of the proximity of the MH ⇆ P + V reaction.

DISCUSSION

Subsystems of $CaO-MgO-SiO_2-CO_2-H_2O$ have been studied at low pressures to define the framework for the complex quinary system. Synthetic carbonatite-like melts were discovered in $CaO-CO_2-H_2O$ [*Wyllie and Tuttle,* 1960], and $CaO-SiO_2-CO_2-H_2O$ [*Wyllie and Haas,* 1965, 1966] was studied as the simplest combination of carbonatite and silicate minerals. These were extended to mantle pressures [*Wyllie and Boettcher,* 1969; *Boettcher and Wyllie,* 1969] to explore the possible links between carbonatites and kimberlites. In both systems, calcite or aragonite is stable to at least 40 kbar in the presence of liquid.

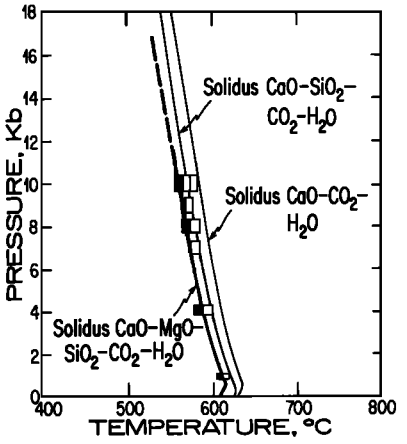

Fig. 2. Pressure-temperature projections of the vapor-saturated solidus in the system $CaO-MgO-SiO_2-CO_2-H_2O$. Experimental results from Table 3 are shown as rectangles. The quaternary solidus is modified from *Boettcher and Wyllie* [1969], and the ternary solidus is modified from *Wyllie and Boettcher* [1969].

To estimate the conditions under which dolomite would crystallize from synthetic carbonatite magma, *Wyllie* [1965] inferred the phase relationships in the system $CaO-MgO-CO_2-H_2O$ on the basis of preliminary experimental data. He deduced that brucite would replace periclase as the primary magnesian phase at a pressure near 1 kbar, and that at higher pressures, the quaternary dissociation reaction for dolomite would intersect the solidus, bringing dolomite into equilibrium with liquid. Our experiments at higher pressures were designed to test the inferred phase relationships, but we found no dolomite (see Table 1). The reason for the nonappearance of dolomite is given by M. F. Fanelli's discovery of a second low-temperature eutectic at 2 kbar, separated from the calcite-portlandite-brucite eutectic by a thermal maximum on the liquidus surface, approximately along the join $CaCO_3-Mg(OH)_2$. At this other eutectic, calcite, dolomite, and periclase are precipitated (M. Fanelli and P. J. Wyllie, unpublished manuscript, 1980).

Some petrological applications to carbonatites of studies in these systems have been discussed in previous publications [e.g., *Wyllie and Tuttle,* 1960; *Franz and Wyllie,* 1967; *Wyllie and Boettcher,* 1969; *Boettcher and Wyllie,* 1969]. It is now established that there are paths on the liquidus of the system $CaO-MgO-SiO_2-CO_2-H_2O$ from high-temperature silicate liquids with small proportions of dissolved CO_2 and H_2O, to lower temperature liquids enriched in CO_2 or H_2O, or both, which precipitate carbonates or hydrous minerals, or both, along with the silicate minerals [*Wyllie and Huang,* 1976; *Eggler,* 1978]. The introduction of carbonates or hydrous minerals onto the liquidus via subsolidus carbonation or hydration reactions produces some intricate phase relationships that change as a function of pressure. One example, for the system $MgO-SiO_2-CO_2-H_2O$, has been described and illustrated in detail by *Ellis and Wyllie* [1980]. The low-temperature solidus curves of Figures 1 and 2, involving hydrous minerals and carbonates, provide necessary boundaries for comprehension of these phase relationships within the model system $CaO-MgO-SiO_2-CO_2-H_2O$ and its subsystems.

Nesbitt and Kelly [1977] have discovered 'primary magmatic inclusions' in monticellite from the Magnet Cove, Arkansas, carbonatite consisting of 50 wt % CaO, 17% CO_2, 16% SiO_2, 11% H_2O, and other components, including 1% MgO. They conclude that the original carbonatite magma was essentially a $CaO-CO_2-H_2O$ liquid, and these compositions are remarkably similar to those of the eutectic liquids in the system $CaO-SiO_2-CO_2-H_2O$. Although these inclusions do contain some MgO, the carbonatite at Magnet Cove is nearly pure calcite ($CaCO_3$) [*Erickson and Blade,* 1963]. Based on our results in the system $CaO-MgO-CO_2-H_2O$ and $CaO-MgO-SiO_2-CO_2-H_2O$, we would not predict the presence of dolomite at Magnet Cove, and such appears to be the case. With a composition richer in MgO, dolomite would occur at depth, as it does at Alnö [*von Eckerman,* 1948]. Hydrous minerals such as brucite and portlandite that coexist with eutectic liquids in our experiments do not occur in carbonatites. However, this is easily explained if the compositions of the vapors, that is, the chemical potentials of H_2O, are buffered at sufficiently low values in the final stages of crystallization [*Wyllie,* 1965].

Thus all of these synthetic carbonatite systems provide a basis for the interpretation of carbonatites as products of crystallization from magmas. The addition of MgO and SiO_2 to the simple ternary system widens our knowledge of the relationship between carbonate and silicate magmatic rocks. This paper is the first to compare the eutectic reactions for all of these systems.

Acknowledgments. A. Gaines greatly assisted us by determining the lattice parameters of the synthetic aragonites. I. S. McCallum kindly analyzed the synthetic aragonites with the electron microprobe. The manuscript was critically reviewed by Robert C. Newton. This work was supported by NSF grants GA-923 and EAR76-20410 to P. J. Wyllie and GA-1364 and EAR78-16413 to A. L. Boettcher. Institute of Geophysics and Planetary Physics, University of California, Los Angeles, contribution 1865.

REFERENCES

Barnes, H. L., and W. G. Ernst, Ideality and ionization in hydrothermal fluids, The system $MgO-H_2O-NaOH$, *Amer. J. Sci., 261,* 129–150, 1963.

Boettcher, A. L., and D. M. Kerrick, Temperature calibration in cold-seal pressure vessels, in *Research Techniques for High Pressure and High Temperature,* edited by G. C. Ulmer, pp. 179–193, Springer, New York, 1971.

Boettcher, A. L., and P. J. Wyllie, The calcite aragonite transition measured in the system $CaO-CO_2-H_2O$, *J. Geol., 76,* 314–330, 1968.

Boettcher, A. L., and P. J. Wyllie, The system $CaO-SiO_2-CO_2-H_2O$, III, Second critical end-point on the melting curve, *Geochim. Cosmochim. Acta, 33,* 611–632, 1969.

Eggler, D. H., The effect of CO_2 upon partial melting of peridotite in the system $Na_2O-CaO-Al_2O_3-MgO-SiO_2-CO_2$ to 35 kb, with an analysis of melting in a peridotite-H_2O-CO_2 system, *Amer. J. Sci., 278,* 305–343, 1978.

Ellis, D. E., and P. J. Wyllie, Phase relations in the system $MgO-SiO_2-H_2O-CO_2$ at pressures up to 100 kbar and petrological implications, *Amer. Mineral., 65,* in press, 1980.

Erickson, R. L., and L. V. Blade, Geochemistry and petrology of the alkalic igneous complex at Magnet Cove, Arkansas, *Geol. Surv. Prof. Pap., 425,* 1963.

Franz, G. W., Melting relationships in the system $CaO-MgO-SiO_2-CO_2-H_2O$: A study of synthetic kimberlites, Ph.D. thesis, Penn. State Univ., University Park, 1965.

Franz, G. W., and P. J. Wyllie, Experimental studies in the system $CaO-MgO-SiO_2-CO_2-H_2O$, in *Ultramafic and Related Rocks,* edited by P. J. Wyllie, pp. 323–326, John Wiley, New York, 1967.

Goldsmith, J. R., and H. C. Heard, Sub-solidus phase relationships in the system $CaCO_3-MgCO_3$, *J. Geol., 69,* 45–74, 1961.

Goldsmith, J. R., and R. C. Newton, P-T-X relations in the system $CaCO_3-MgCO_3$ at high temperatures and pressures, *Amer. J. Sci., 267-A,* 160–190, 1969.

Luth, W. C., and C. O. Ingamells, Gel preparation of starting materials for hydrothermal investigation, *Amer. Mineral., 50,* 225–258, 1965.

Nesbitt, B. E., and W. C. Kelly, Magmatic and hydrothermal inclusions in carbonatite of the Magnet Cove complex, Arkansas, *Contrib. Mineral. Petrol., 63,* 271–294, 1977.

Sharp, W., and G. C. Kennedy, The system CaO-CO_2-H_2O in the two-phase region calcite + aqueous solution, *J. Geol., 73,* 391–403, 1965.

Takenouchi, S., and G. C. Kennedy, The binary system H_2O-CO_2 at high temperatures and pressures, *Amer. J. Sci., 262,* 1055–1074, 1964.

von Eckerman, H., The alkaline district of Alnö Island, *Sver. Geol. Unders., Ser. C, 36,* 1948.

Wyllie, P. J., Melting relationships in the system CaO-MgO-CO_2-H_2O, with petrological applications, *J. Petrol., 6,* 101–123, 1965.

Wyllie, P. J., and A. L. Boettcher, Liquidus phase relationships in the system CaO-CO_2-H_2O to 40 kilobars pressure, with petrological applications, *Amer. J. Sci., 267-A,* 489–508, 1969.

Wyllie, P. J., and J. L. Haas, The system CaO-SiO_2-CO_2-H_2O, I, Melting relationships with excess vapor at 1 kilobar pressure, *Geochim. Cosmochim. Acta, 29,* 871–893, 1965.

Wyllie, P. J., and J. L. Haas, The system CaO-SiO_2-CO_2-H_2O, II, The petrogenetic model, *Geochim. Cosmochim. Acta, 30,* 525–543, 1966.

Wyllie, P. J., and W. L. Huang, Carbonation and melting reactions in the system CaO-MgO-SiO_2-CO_2 at mantle pressures with geophysical and petrological applications, *Contrib. Mineral. Petrol., 54,* 79–107, 1976.

Wyllie, P. J., and O. F. Tuttle, The system CaO-CO_2-H_2O and the origin of carbonatites, *J. Petrol., 1,* 1–96, 1960.

(Received March 20, 1980;
revised April 22, 1980;
accepted May 9, 1980.)